

Organic carbon and carbon isotopes in modern and 100-year-old-soil archives of the Russian steppe

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Abstract

Archived soils can provide valuable information about changes in the carbon and carbon isotope content of soils during the past century. We characterized soil carbon dynamics in a Russian steppe preserve using a 100-year-old-soil archive and modern samples collected from the same site. The site has been protected since 1885 to the present, during which time the region has experienced widespread conversion to cultivation, a decrease in fire frequency, and a trend of increasing precipitation. In the preserve, the amount of organic carbon did not change appreciably between the 1900 and 1997 sampling dates, with 32 kg C/m² in the top meter and a third of that in the top 20 cm. Carbon and nitrogen stocks varied by less than 6% between two replicate modern soil pits or between the modern sites and the archive. Radiocarbon content decreased with depth in all sites and the modern SOM had positive Δ values near the surface due to nuclear weapons testing in the early 1960s. In the upper 10 cm, most of the SOM had a turnover time of 6–10 years, according to a model fit to the radiocarbon content. Below about 10 cm, the organic matter was almost all passive material with long (millennial) turnover times. Soil respiration $\Delta^{14}\text{CO}_2$ on a summer day was 106–109‰, an isotopic disequilibrium of about 9‰ relative to atmospheric $^{14}\text{CO}_2$. In both the modern and archive soil, the relative abundance of ^{13}C in organic matter increased with depth by 2‰ in the upper meter from $\delta^{13}\text{C} = -26\text{‰}$ at 5 cm to -24‰ below a meter. In addition, the slope of $\delta^{13}\text{C}$ vs. depth below 5 cm was the same for both soils. Given the age of the soil archive, these results give clear evidence that the depth gradients are not due to depletion of atmospheric $^{13}\text{CO}_2$ by fossil fuel emissions but must instead be caused by isotopic fractionation between plant litter inputs and preservation of SOM. Overall, the data show that these soils have a large reservoir of recalcitrant C and stocks had not changed between sampling dates 100 years apart.

Keywords: ^{13}C , ^{14}C , grassland, land use, organic matter, sequestration, prairie

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Introduction

The Russian plains contain some of the most carbon-rich soils in the world, including vast expanses of tall- and short-grass prairie Chernozems (Mollisols, Fig. 1, Afanas'eva, 1966). Cultivation of steppe over the past century has caused large losses of soil carbon (Kolchugina *et al.*, 1995; Sherbakov & Vaseneva, 1996), according to

observations of carbon content in cultivated and uncultivated lands. However, there has been little quantification of changes in carbon storage in uncultivated ecosystems over the period, or the turnover time of soil organic matter (SOM, Chichagova & Cherkinsky, 1993). These data are needed to assess how much carbon storage has changed over the past century in sites that have not undergone land use change and to understand how land use effects compare to other trends.

Carbon isotopes in SOM can elucidate soil carbon cycling and are useful as constraints for local and global carbon models (Balesdent *et al.*, 1987; Nadelhoffer & Fry, 1988; Ciais *et al.*, 1995; Trumbore, 1997). In unmanaged

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Fig. 1 Map of Russia showing the historic range of steppe (gray shading) and location of Kamennaya Steppe Preserve (site of Dukachaev Institute), near the city of Voronezh. Both the forest steppe (light gray) and steppe (dark gray) zones were historically more than 85% grassland.

soils, organic matter typically increases in $^{13}\text{C}/^{12}\text{C}$ and decreases in $^{14}\text{C}/^{12}\text{C}$ content with depth (Nadelhoffer & Fry, 1988; Goh *et al.*, 1977; Trumbore & Torn, in press). The radiocarbon content of SOM provides information about the rate at which organic material cycles through the soil and the time since the material was fixed by plants. Thus, the decrease in radiocarbon with depth reflects progressively older organic matter (Goh *et al.*, 1977). Modeling with radiocarbon is a useful tool for estimating the turnover time of SOM. In addition to using radioactive decay to estimate the residence time of material with century-millennial turnover times, the incorporation of ^{14}C created by high energy particles released by above-ground nuclear weapons tests (1959–1963), known as the bomb spike, is a measure of the carbon cycling on decadal timescales (Goh *et al.*, 1976). Modeling the bomb spike is especially effective if soil archives are available so that ^{14}C in soils sampled several decades apart can be compared (e.g., Trumbore *et al.*, 1996; Richter *et al.*, 1999).

In contrast to soil ^{14}C , the controls of soil ^{13}C distributions are less well understood. In systems of unchanging vegetation, two mechanisms are often proposed to explain the trend of increasing ^{13}C abundance with depth: fractionation during stabilization of organic matter and reduction in atmospheric and plant ^{13}C by fossil fuel emissions. Fractionation during stabilization of organic matter could occur through preferential metabolism of the lighter C isotope by microbes, preferential stabilization of compounds that are enriched in ^{13}C , or downward movement of ^{13}C -enriched material to lower horizons (Nadelhoffer & Fry, 1988). There is some evidence for the first two mechanisms, but their magnitude has not been measured directly. At the same time, the effect of fossil fuel emissions is also consistent with the observed soil trend. Fossil carbon emissions, which have low $^{13}\text{C}/^{12}\text{C}$ ratios, have made atmospheric $\delta^{13}\text{C}$ more negative. As a result, recently fixed organic material is isotopically lighter than older material and, as shown

by the ^{14}C evidence, the older material is found deeper in the soil.

Evaluating the influence of the fossil signal vs. the fractionation in stabilization is difficult because they are confounded in modern soils. Soil samples collected before the atmosphere was strongly influenced by fossil fuels could allow us to isolate the biological fractionation processes in soil C cycling. Archives ≥ 100 -year-old should be adequate for this purpose, since almost all the decrease in atmospheric $\delta^{13}\text{C}\text{O}_2$ occurred in the past century. The change in atmospheric $\delta^{13}\text{C}\text{O}_2$ was less than 0.4‰ between 1700 and 1900, but was 1.3‰ in the last 100 years (Francey *et al.*, 1999).

It is important to understand the controls of ^{13}C in SOM, as this would allow us to better characterize the processes of carbon stabilization in soil and to predict the $\delta^{13}\text{C}\text{O}_2$ signature of soil respiration. Predicting respired $\delta^{13}\text{C}\text{O}_2$ accurately is important to estimating global carbon fluxes. For example, in some inverse carbon models, a 0.2‰ difference in the $\delta^{13}\text{C}\text{O}_2$ value of respiration can cause a 0.5 Gt/y difference in the estimate of terrestrial C sequestration (Fung *et al.*, 1997).

The recent discovery of well-documented soil archives for the Russian plains, the Historic Russian Soil Collection (HRSC) collected in 1895–1903, creates the opportunity to document long-term trends in C, ^{13}C , and ^{14}C in undisturbed and managed ecosystems (Lapenis *et al.*, 2000). These archived monoliths include the soil to at least a meter depth, so they allow an estimate of C dynamics in deeper soil horizons. Using the original sampling notes, we matched a 100-year-old soil archive of moist steppe (tall grass prairie; Fig. 2) to its source site (Lapenis *et al.*, 2000). Protected within the Kamennaya Steppe National Park, the site has been maintained under consistent management of extremely light grazing with no plowing or planting in the intervening years (Shapovalov, 1969). Changes in the surrounding environment, in fire frequency, climate, and hedgerows (windbreak forests bordering fields), are described under Site Description.



Fig. 2 Photo of the Historic Russian Soil Collection (HRSC) #32 archive monolith of steppe soil. The letters a and b indicate the top and bottom half of monolith, respectively.

In 1995 and 1997 we re-sampled the steppe soil archive and its source site, respectively. Our goals were to determine changes in carbon stocks over the past century under preserve management and to compare the depth profiles of carbon isotopes (^{13}C and ^{14}C) between the archive and modern soils.

Site description

We studied soils in the moist Central Chernozem Region of Russia, ~200 km east of the city of Voronezh (Bobrov's administrative district; Fig. 1). The study sites were protected within the Dukachaev Institute which is located in the Kamennaya Steppe National Park, a ~5000-ha watershed, isolated by the Chigla and Talovaya rivers. Elevation is 200 m with gradual relief within the preserve. Mean annual temperature is 6.4°C. Mean annual precipitation has increased during the past century in this region. Currently, annual precipitation averages 520 mm (~25% as snow) and snow cover lasts roughly 100 days. At the beginning of the 20th century, mean annual precipitation was ~430 mm (Ivanov, 1991). Most of the increase occurred in winter precipitation (Ivanov, 1991). Summer drought remains common and soil moisture reaches field capacity only during late spring. The water table varies seasonally, from 2 m below the surface in April to 5 m in mid winter. Water table depth has changed concurrently with the trend in precipitation,

with mean annual water table rising from ~7 m below the surface 100 years ago to ~3 m at present (Ivanov, 1991). Grassland in this climate was called meadow steppe by Parton *et al.* (1993) in their modeling study of soil C cycling. The region's grasslands are also known as Kamennaya steppe.

The parent material of the Kamennaya region is brown-yellow carbonate loess and clay thought to have been deposited ~4500–6000 years ago during the mid-Holocene (Ivanov, 1991). Most Kamennaya Steppe soils are categorized as either Common or Meadow-Chernozems. Soil pH in water is 6.9 in the A horizon, 7.3 in the AB horizon, and 9.05 in the B horizon at the modern site 1 (Table 1). The pH in 1 M KCl is 7.2 (A horizon), 7.7 (AB horizon) and 8.6 (B horizon). The carbonate content in the A horizon is less than 0.1% by mass.

The soil archive HRSC monolith #32 is labeled 'Kamennaya Steppe, Talovaya preserve.' Currently, Talovaya preserve comprises 24 ha in two areas (preserves #1 and #2), located 0.7 km apart. Prior to protection, fields in this region were periodically grazed and burned. Vegetation was not managed (i.e., nothing was seeded) or tilled. Since establishment in 1882–1885, the preserve areas have been protected from tillage, grazing, and other land management changes that are now prevalent in the region (Shapovalov, 1969). Fire frequency has been reduced in the region and the preserve compared to before 1900. Dukachaev implemented the planting of forest windbreaks (hedgerows) on the borders of fields in the Dukachaev Institute area. The increase in local tree density is reflected in more arboreal pollen in the surface of the modern soil compared to the archive (Andreev, 2001).

The preserve sites are characterized as moist Tipchak (fescue or feathergrass) steppe, analogous to the tall grass prairie of North America. Tipchak steppe was historically widespread in Russia, covering about $1.5 \times 10^6 \text{ km}^2$ (Fig. 1). The vegetation is mainly herbaceous perennials with some encroachment of woody perennials. The dominant species inside the preserved steppe area were *Festuca sulcata* with *Knautia arvensis* (height 45–85 cm), *Veronica spicata* (15–20 cm) and *Sedum acre* (2–5 cm) (Pashenko, 1997; Shapovalov, 1969). Above-ground plant biomass is 100–120 g dry wt/m². All of the plant species identified from 1970 to 1992 use C_3 photosynthesis and no large changes in relative species abundance have been documented (Pashenko, 1997; Shapovalov, 1969). Pollen analysis of the archive soil confirms that historic plant species also employed C_3 pathways. Therefore, the $\delta^{13}\text{C}$ signature of plant inputs is expected to be roughly -27‰ , and there is no evidence for historical change in the isotopic content of plant inputs.

Methods

Archive sampling

The HRSC monolith #32 was collected sometime between 1895 and 1903 by a Russian soil scientist, Dr Rizpolozhensky, and purchased by the St. Petersburg Academy of Forestry in 1903 where it is still stored (Fig. 2). The intact monolith was air dried and stored horizontally in two wooden cases with glass fronts. It was not exposed to resins. The location of the sampled site and the methods of collection were detailed in the field logs left by Rizpolozhensky (Lapenis *et al.*, 2000). These sampling notes were used to re-locate the original source site for re-sampling. In March 1995, the archive was sampled by collecting a ~5-cm wide strip that ran the length of the right-hand margin of the monolith and extended roughly 2.5 cm towards the back of monolith. The archive did not have an intact litter layer. There were a few individual pieces of plant material or litter that had been compressed at the top of the profile and these were included with the uppermost A horizon sample.

Modern soil sampling

In August 1997, we sampled the two preserve sites of Kamennaya steppe. A portion of preserve #2 was burned in 1986. We sampled outside the burned area. The archive field notes for monolith #32 state that the monolith was taken inside the 'microplateau'. Each preserve area has a few ha that could be classified as a microplateau. According to senior researchers at the Institute, the original monolith was taken from preserve #1. The soil pit locations are sites 1 and 2 in preserves #1 and #2, respectively.

Soil pits were dug 2 m deep. Carbon samples were collected from the wall of the pit by channel sampling each soil horizon, starting at the bottom of the pit (i.e., we collected a rectangular channel of soil running the entire thickness of the horizon). The litter layer was collected by gently raking by hand a known area of the surface. Soil and litter samples were sealed in plastic bags in the field and stored in a cool environment while in transit, and then refrigerated in the United States until being oven-dried at 70 °C.

In all results presented here, the soil depth of 0 cm corresponds to the top of the first mineral A horizon. Increasing depth is positive and the litter layer above the A horizon is a negative depth.

Soil C and N analysis

All soils used for C, N, and isotope analysis were oven-dried, sieved (2 mm), and pretreated with acid to remove

carbonates (Carter, 1993). Only soils from below 50 cm showed signs of carbonate effervescence. There were almost no stones greater than 2 mm in archive or modern soil. The %C and %N of soil was measured with a Carlo Erba or Fisons nitrogen and carbon elemental analyzer. We estimate the measurement error to be less than 5%. The standard deviation of 12 replicate peach leaf standards was less than 0.5% of the standard value; standard deviation of duplicate soils samples was less than 4%. There was a similar mass of C in the standards and samples.

^{14}C of soil respired CO_2

A PVC base was put into the soil and plants were clipped to the top of the litter layer 8 and 13 h before sampling for sites 1 and 2, respectively. Soil respired CO_2 was trapped on 13 August 1997, according to methods described by Gaudinski *et al.* (2000). For sampling, a closed dynamic chamber, plumbed to circulate the chamber headspace into a series of traps, was placed on the base. The chamber headspace was first scrubbed of CO_2 by pumping air through a soda lime trap for 30 min. Over a subsequent 60-min interval, the headspace air was passed through a desiccant and a trap filled with molecular sieve (mesh size 13×) that adsorbs CO_2 . In October 1997, the CO_2 was baked off the trap (Bauer *et al.*, 1992) and analyzed for ^{14}C and ^{13}C content. The $^{14}\text{CO}_2$ of respiration was calculated by correcting the measured value for the initial content of ambient air in the chamber using a mass balance equation and assuming that the $\delta^{13}\text{CO}_2$ of respiration and the atmosphere were -26‰ and -8‰ , respectively.

^{13}C of Soil C and CO_2

The ^{13}C content of ground soil samples was analyzed with an elemental analyzer (Carlo Erba or Fisons) interfaced with a mass spectrometer (Micromass Optima or Finnegan Mat). For soil respiration and selected solid samples, a split of combusted CO_2 (from soils prepared for ^{14}C analysis) was cryogenically purified and analyzed for ^{13}C content with a dual inlet isotope ratio mass spectrometer. Carbonate was removed from the soils used for ^{14}C analysis (and some duplicate ^{13}C measurements) by incubating a thin layer of soils in a glass vacuum dessicator with a beaker of hydrochloric acid (*Sensu* Harris *et al.*, 2001).

The method of sample preparation and analytical method had a negligible effect on the ^{13}C values. We tested for the effect of the method of carbonate removal (exposure of soil to acidic fumes or acidic solution) and the method of preparing ^{13}C samples (combusting solid

Table 1 Soil descriptions. The soil depth of 0 cm corresponds to the top of the first mineral A horizon. The litter layer above that is a negative depth

Depth (cm)	Horizon in field [†]	Bulk density (g/cm ³)	pH		Soil description [‡]
			(H ₂ O)	(KCl)	
Archive, sampled ~1900					
0–5	A	0.52	7.48	6.51	A horizon, many fine roots, Blocky aggregation, very dark color
5–12	A	0.68	6.85	6.45	A horizon, many fine roots, Blocky aggregation, very dark color
12–20	A	0.73	7.24	6.66	A horizon, many fine roots, Blocky aggregation, very dark color
20–36	A	0.86	7.21	6.51	A horizon Blocky aggregation, very dark color
36–50	A	0.85	7.29	6.58	A horizon Blocky aggregation, very dark color
50–65	AB	1.12	7.74	6.61	A horizon Blocky aggregation, very dark color
65–78	B	1.17			AB horizon, mixed Organic stains along ped faces Abrupt boundary
78–100	B	1.23			Bca horizon, carbonates present Filled burrows (krotovinas) dark in color
100–120	B	1.24	8.61	7.68	Bca horizon, carbonates present Filled burrows (krotovinas) dark in color
120–134	B/C	1.32	7.79	7.42	Cca horizon; carbonates present; weak blocky structure with little organic staining
Modern Site 1, sampled 1997					
–5–0	Ao ^A	0.13	6.64	6.15	Litter layer; recognizable plant parts
0–5	A	0.52	6.63	6.11	Strong, fine granular structure Loam. Non-sticky, non-plastic consistence 10YR2/1 – moist color
5–13	A	0.82	6.88	6.25	Fine-medium granular structure Clay-loam. Slightly sticky, plastic sticky consistence 10 YR2/1 – moist color
13–21	A	0.84	7.04	6.39	Very strong, medium angular blocky structure Loam. Slightly sticky, slightly plastic consistence 10YR2/1 – moist color
21–37	A	0.86			Strong medium-fine granular structure Loam. Slightly sticky consistence 10YR3/1 – moist color
37–45	A	0.99	7.06	6.43	Loam. Slightly sticky consistence 10YR3/1 – dry, 10YR2/1 – moist color
45–53	AB	1.12	7.34	6.59	Strong, medium granular structure Loam with more clay than above. Sticky consistence 10YR3/1 – dry, 10YR 2/1 – moist color
53–68	AB	1.32			Strong, fine subangular blocky structure Clay loam. Sticky and plastic consistence 10YR3/1 – 4/1 moist color
68–90	AB	1.32			Strong coarse subangular blocky structure Clay loam. Sticky and plastic consistence 10YR4/3-d, 10YR4/2-m.
90–107	B	1.32	9.05	8.46	Clay loam. Sticky and plastic consistence 10YR4/3 moist color
107–130	B	1.32		8.54	Clay loam; sticky, very plastic consistence 10–7.5YR5/4 moist color

Depth (cm)	Horizon in field [†]	Bulk density (g/cm ³)	pH		Soil description [‡]
			(H ₂ O)	(KCl)	
Modern site 2, sampled 1997					
–3–0	Ao ^A	0.13			
0–5	A ₁	0.61			
5–12	A	0.68			
12–20	A	0.73			
20–36	A	0.72			
36–50	A	0.85			
50–58	AB	1.01			
58–75	AB	1.17			
75–82	B	1.2			
82–102	B	1.23			
102–122	B	1.24			
122–142	B	1.24			

*Soil pH was measured for the archive and dried modern soil in 1998.

[†]The horizon designations in this column were made in the field at the time of sample collection. For the archive, they were made by Boach *et al.* (1903). The Russian horizon designation Ao^A corresponds to a grassland or meadow litter (O) horizon.

[‡]The archive description was made at the Academy of Forestry, St. Petersburg, 1995, by J. Harden and A. Timofeev. In addition, Boach *et al.* (1903) measured texture and humus (OM) content at two depths when the monolith was collected. For 0–26 cm: humus = 110 g/kg, sand = 670 g/kg, silt = 87 g/kg. For 87–101 cm: humus = 10 g/kg, sand = 600 g/kg, silt = 93 g/kg. Textures are reported according to the USDA Textural Classification System, sand > 0.05 mm; 0.002 < silt < 0.05 mm; clay is remainder by difference. The modern soil was described in the field and at USGS, Menlo Park, 1997, by J. Harden, A. Timofeev, and M. Torn.

soil in the elemental analyzer or combusting purified CO₂ on the vacuum line before direct mass spectrometer injection). For the five samples analyzed by all combinations of methods, the average difference between values was 0.1‰. This is within the analytical error in the isotope measurements.

Bulk density

Bulk density was determined for the 1997 soil pits from the dry weight of cores of known volume. Cores were collected in every horizon to 1.3 m. Bulk density was not measured in the archival soil monolith. Instead, we assumed that its bulk density was the same as that of the corresponding horizon in the modern samples. There was a close match between the modern and archived soils for both %C and thickness of all horizons, supporting the assumption that soil density was comparable. Bulk density is used in the calculations of total C content (kg/m²) but is not needed in comparisons of carbon density or isotopic ratios.

Radiocarbon analysis

The radiocarbon content of SOM was measured by Accelerator Mass Spectrometry (AMS) at Lawrence Livermore National Laboratory (LLNL). The graphite AMS targets were prepared by oxidizing SOM to CO₂

by sealed-tube combustion with cupric oxide followed by reduction of the cryogenically purified CO₂ to graphite by hydrogen or zinc reduction (Vogel *et al.*, 1984). Analytical precision was reported by LLNL to be ± 4–8‰. The Δ¹⁴C unit is normalized such that for the pre-1950 atmosphere, Δ¹⁴C = 0 (Stuiver & Polach, 1977). Positive values of Δ¹⁴C indicate the presence of bomb-produced ¹⁴C, and negative values indicate the predominance of C fixed from the atmosphere long enough ago for significant radioactive decay of ¹⁴C (half-life = 5730 years) to have occurred.

Atmospheric thermonuclear weapons testing from 1959 to 1963 approximately doubled the amount of ¹⁴C in the atmosphere, providing a global isotopic tracer for the C cycle (Fig. 3, Goh *et al.*, 1976). The amount of bomb ¹⁴C that has accumulated in SOM provides a direct measure of the amount of fast-cycling (active + intermediate) C in the soil, i.e., addressing turnover timescales of ~5–100 years (Trumbore & Torn, in press). A straightforward approach to using this signal is to compare ¹⁴C of soils sampled prior to 1960 with contemporary samples from the same location. This method is illustrated in Fig. 3; the turnover times and proportion of C in different pools are adjusted until the model predicts the measured ¹⁴C value in both the modern and archive soils. This may be done with bulk (i.e., unfractionated) soil (Harrison, 1996) as in this study or with fractionated SOM for higher resolution (Trumbore & Zheng, 1996).

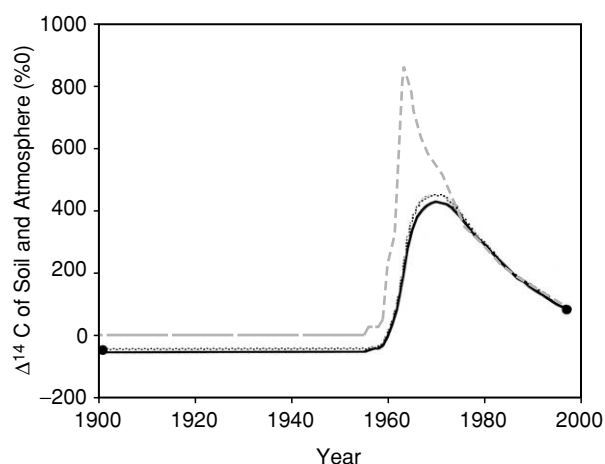


Fig. 3 Atmospheric $^{14}\text{CO}_2$ (dashed gray line) and a comparison of model predictions with measurements of radiocarbon for the top 0–5 cm of mineral soil (A_1 horizon). Solid circles = measured values of $\Delta^{14}\text{C}$ in the soil archive and modern SOM. Solid black line = model predictions parameterized using the deep horizons as a proxy for the passive C at the surface (modeling case 2). Stippled black line = model predictions parameterized with the Century model result that 33% of soil C was in the passive pool (case 1). The modeling cases and results are described in the Modeling and Results sections, respectively.

Modeling approach

We estimated the turnover times of C in the A horizon using a time-dependent, first-order box model of the ^{14}C content of soil C, with three boxes (i.e., homogeneous pools) representing C with annual, decadal, and century/millennial turnover times. These are referred to as the active, intermediate, and passive C pools, respectively (Parton *et al.*, 1987). The model was initialized in steady state and integrated over the time interval between soil collection dates (1900–1997). The amount of C in each pool was assumed to be at steady state because the total carbon stock had not changed. Plant inputs and SOM decomposition rates were assumed to be in steady state although either may have been affected by trends in precipitation and the addition of windbreaks. The radiocarbon content of the atmosphere and soil C changed with time due to above-ground nuclear weapons testing.

The model had the following mass balance constraints:

$$C_{\text{total}} = C_{\text{active}} + C_{\text{intermediate}} + C_{\text{passive}} \quad (1)$$

$$C_{\text{total}}R_{\text{total}} = R_{\text{active}}C_{\text{active}} + R_{\text{intermediate}}C_{\text{intermediate}} + R_{\text{passive}}C_{\text{passive}} \quad (2)$$

where C_{pool} was the fraction of C in a given pool; R_{pool} was the ^{14}C ratio (fraction modern) in a given pool. C_{active} was assumed to be 3% of SOM (Torn, in preparation) and

Table 2 Modeling turnover time and C pool partitioning with ^{14}C : summary of parameters that are fit to data or fixed *a priori*. C = carbon; T = turnover time. Subscript denotes the C pool

Parameter	Case 1*	Case 2†
C_{active}	3% of C	3% of C
$C_{\text{intermediate}}$	64% of C	Fit
C_{passive}	33% of C	Fit
T_{active}	1 y	1 y
$T_{\text{intermediate}}$	Fit	Fit
T_{passive}	Fit	T_{deep} (modeled as a single pool of C)

*Case 1: Amount of passive carbon and turnover time of active carbon based on Parton *et al.* (1987). Amount of active C from Torn, in preparation.

†Case 2: Approach to estimating turnover time of passive C from Harrison *et al.* (1995) in which the lowest B horizon SOM is used to parameterize the passive pool for all horizons, and active C as in case 1.

R_{active} was assumed to correspond to annual turnover. R_{total} was measured; $R_{\text{intermediate}}$ was solved for by modeling. The modeling or parameterization of C_{passive} , $C_{\text{intermediate}}$ and R_{passive} is given in Table 2.

The model was integrated for ^{14}C content using the following equation for each pool:

$$R_i = R_{i-1}(1 - \Delta t(\lambda - 1/\tau)) + (R_{\text{atm},i-1})\Delta t/\tau \quad (3)$$

where the timestep (Δt) was annual; R_i = the ^{14}C ratio of SOM in year i ; λ = radioactive decay rate of ^{14}C ; τ = turnover time, which is the reciprocal of decay rate.

The data inputs—atmospheric $^{14}\text{CO}_2$ and the ^{14}C content of C_{total} in 1900 and 1997—were not sufficient to fully constrain the model formulation described above. Rather, we used two scenarios of reasonable *a priori* constraints to solve for the intermediate pool turnover time and amount (Table 2). In both cases, the active pool of SOM was defined as having annual turnover and making up 3% of total C (Torn, in preparation). In the first scenario (case 1), we set the passive C at 33% as estimated by a Century model simulation for this region (the vicinity of Kursk, Parton *et al.*, 1993), and solved for the best fit turnover times of passive and intermediate C (Table 2). In case 2, we assumed that the turnover time of the passive C was the same in each horizon and could be approximated by the turnover time of SOM in the deepest B horizon (Harrison *et al.*, 1995). We solved for the best fit of partitioning between intermediate and passive C, and the turnover time of intermediate C (Table 2). The assumption that the C in the deepest horizon is passive was supported by the radiocarbon depletion in the B horizons (e.g., radiocarbon ages of 9000–10 000 years), as well as the similarity between archival and modern radiocarbon content at depth

(e.g., $\Delta^{14}\text{C} = -672\text{‰}$ at 100–120 cm depth in the archive and -762‰ at 105–125 cm depth in site 1). The assumption that all passive C had the same turnover time ignores the extent to which the turnover time of passive C varies due to changes in mineralogy or other stabilization mechanisms with depth. The *amount* of passive C was not assumed constant with depth, because soil mineral abundance is correlated with stabilized C (Goh *et al.*, 1976; Oades, 1988; Torn *et al.*, 1997).

Results

Table 1 summarizes soil characteristics for the archive and modern soils. The type and thickness of all horizons was comparable between the three profiles, except that the modern soil had a 3–5 cm thick litter layer that was absent from the archive. Chernozems do not typically have well-developed litter layers because of frequent fires and the litter material in the archived soil may have been compressed by the sampling mechanisms (e.g., Lapenis *et al.*, 2000). There may have been accumulation of litter material over the past 100 years, for example because preserve management reduced fire frequency and grazing compared to that during the decades before the original soil sampling *ca.* 1900.

Total carbon and nitrogen

The organic carbon and nitrogen content were determined for each horizon and summed over the soil profile to 1.4 m (Table 3). Carbon concentrations were similar between the archive and the two modern pits (Fig. 4) and the total carbon and nitrogen contents of the soils were remarkably similar. The carbon stock in the top 20 cm and total profile C varied by less than 6% between the two modern sites or between the modern soil and the archive. The difference in nitrogen content or C:N ratio was not significant (i.e., difference was less than analytical error). The soils contain 32–33 kg C/m², with one-third of that in the top 20 cm and two-thirds below that level. The C:N ratio was 11 in the top 20 cm and whole profile of both modern and archived soil samples.

¹³C depth profiles

In the modern soils, the $\delta^{13}\text{C}$ value in the litter layer was 1–2‰ more negative than in the mineral horizons, presumably due to the fossil fuel dilution of ¹³C in the atmosphere and plant inputs (Fig. 5). Below 3–5 cm, there was no apparent difference in the ¹³C-depth profile between the modern and archive soil. The ¹³C/¹²C ratio of SOM increased with depth in both soils, averaging -26‰ just below the litter layer and increasing to -24‰ below a meter in the profile. In the modern and archived soils, the depth profile had the same, significantly non-zero slope. For regression with all depths for

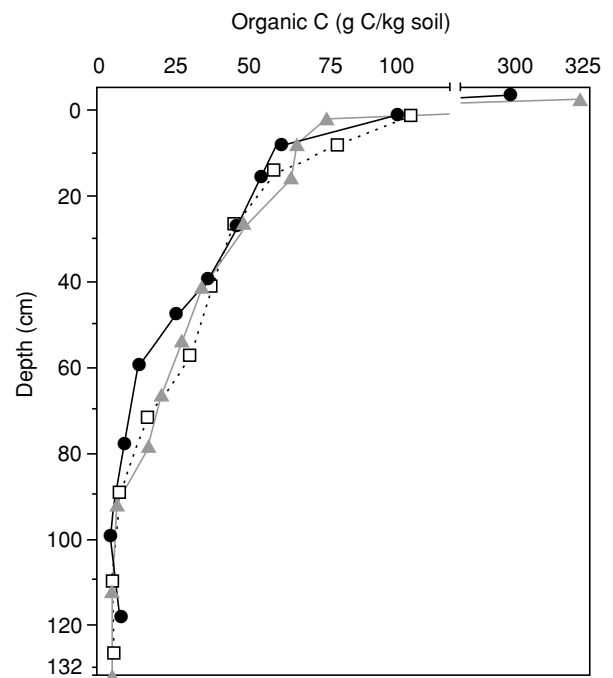


Fig. 4 Depth profile of %C for archive soils and 1997 soils. The top of the first mineral horizon is the 0 cm depth. Litter is negative depth. Legend: open black squares and dashed lines are archive; Solid black circles and lines are modern site 1; solid gray triangles and lines are modern site 2.

Table 3 Carbon and nitrogen content of steppe soil from HRSC#32 archive and co-located modern samples

Soil	Carbon (kg C/m ²)			Nitrogen (kg C/m ²)		
	Archive	Modern site 1	Modern site 2	Archive	Modern site 1	Modern site 2
Litter		1.3	1.9		0.1	0.2
Top 20 cm	10.1	9.5	9.9	0.9	0.8	0.9
1.4 m profile excluding litter	33.1	31.3	30.3	3.0	2.7	2.7
1.4 m profile including litter	33.1	32.5	32.2	3.0	2.9	2.9

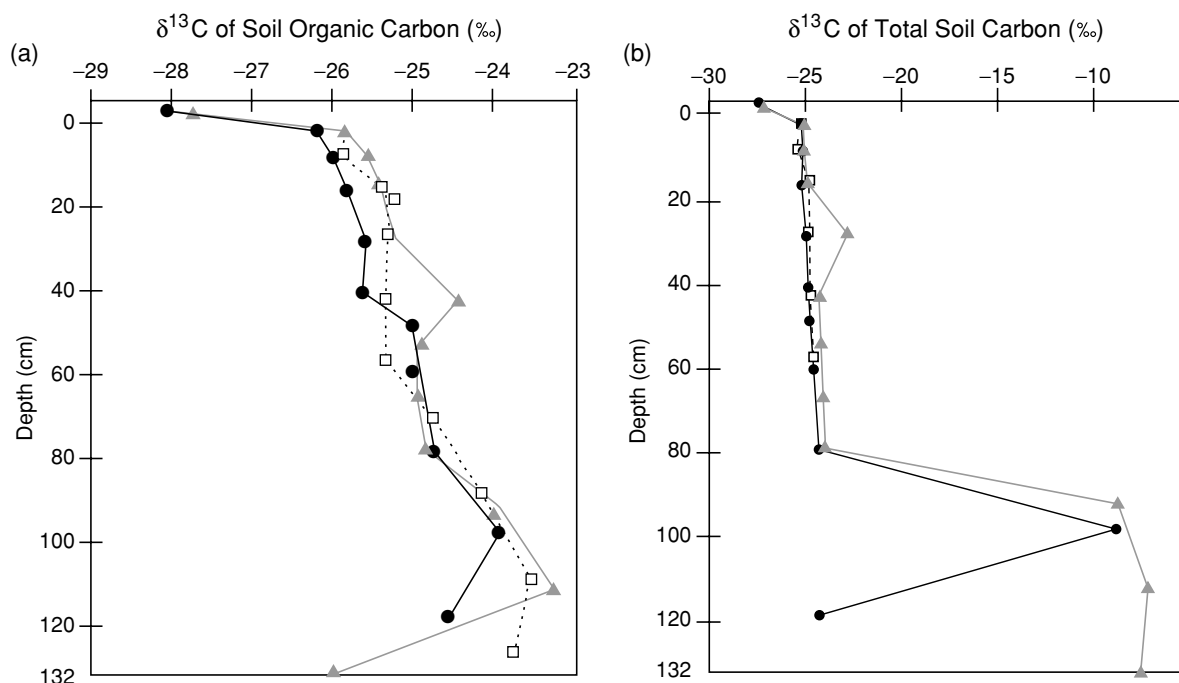


Fig. 5 Depth profile of $\delta^{13}\text{C}$ for archive soils and 1997 soils for (a) organic carbon only (carbonate removed) and (b) for total carbon (no carbonate removal). The top of the first mineral horizon is the 0 cm depth. Litter is negative depth. Legend as in Fig. 4.

the archive and modern site 1, and for all but the deepest sample for modern site 2, y -intercept = -26‰ , slope = $0.02\text{‰}/\text{cm}$, $P < 0.001$. Including the deepest sample at modern site 2 gives y -intercept = -26‰ , slope = $0.01\text{‰}/\text{cm}$, $P < 0.07$.

^{14}C depth profiles

The ^{14}C content measured in the archived soils has been converted to the $\Delta^{14}\text{C}$ that the soil would have had if analyzed in 1900 rather than after years of storage (i.e., we back-calculated the radiocarbon content the archive soil had in 1900 based on its 1998 value and the amount of radioactive decay that would have occurred in 98 years). The radiocarbon content of SOM decreased with depth in both the archive and the modern soil profiles (Fig. 6). This shows that soil carbon is more stable and more isolated from plant inputs with increasing soil depth. The highly depleted carbon below 1 m indicates turnover times of 10 000 years, whereas the loess deposit underlying the soil has an estimated age of 4500–6000 years. This may mean that the loess deposit contains older C that is contributing to the depleted signature. In addition, when the amount of time that soil carbon has been building up (i.e., the age of the parent material) is short relative to the turnover time, it

is likely that the soils have not yet reached an equilibrium level of C storage.

The two uppermost horizons of the modern soil (O and A_1 horizons) had positive $\Delta^{14}\text{C}$ values due to incorporation of 'bomb C', indicating that those horizons are dominated by organic matter fixed in the past three decades (i.e., that cycles on decadal timescales). Because the archive did not have a litter layer (O horizon), there was only one horizon, the A_1 , for which there was a bomb spike sample paired with the same horizon in the archive for modeling turnover.

Only a limited number of turnover time scenarios could predict the measured ^{14}C values for both modern and archive A_1 samples (Fig. 3). The model result for case 2, in which we used the deepest soil horizon to characterize the turnover time of passive C, indicated 89% intermediate C with a turnover time of 6 years and 9% passive C with a turnover time of 10 000 years (Fig. 3). For case 1, in which we used the estimate of passive C (33%) generated by a Century simulation for Russian meadow grasslands (Parton *et al.*, 1993), the model indicated roughly the same turnover time for the intermediate cycling C as it did for case 2, but a lower quantity of intermediate cycling. The best fit to our model in case 1 was a soil with 65% intermediate C with a turnover time of 10 years and 33% passive C with a turnover time of 1300 years.

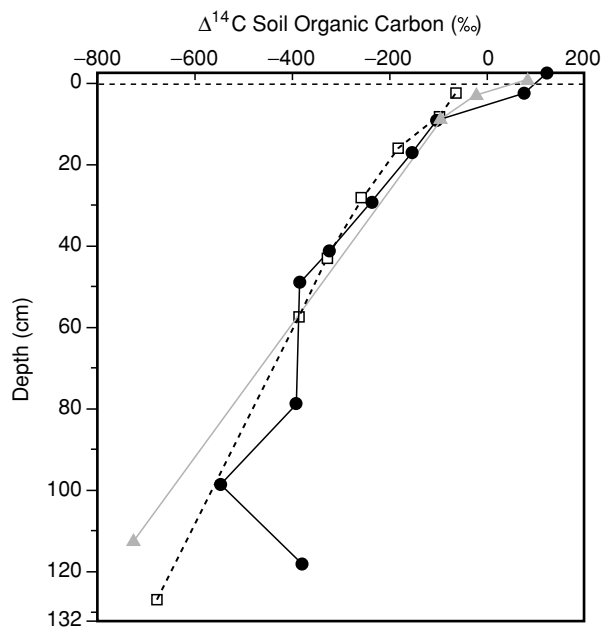


Fig. 6 Depth profile of $\Delta^{14}\text{C}$ for archive soils and 1997 soils. The top of the first mineral horizon is the 0 cm depth. Litter is negative depth. Legend as in Fig. 4.

Below 10 cm, the radiocarbon profiles of the archive and modern soils were roughly the same. The lack of bomb radiocarbon was consistent with the ^{13}C data, in which the modern atmospheric signal was not detectable below 10 cm. However, there was no straightforward way to constrain a multi-pool model of radiocarbon cycling in the bulk soil of these horizons.

^{14}C of soil respiration

The $\Delta^{14}\text{C}$ of respired CO_2 was 106‰ and 109‰ for the two replicates measured with the respiration chamber (one per site) in August 1997. The isotopic disequilibrium of soil respired $^{14}\text{CO}_2$ was roughly 9‰ relative to atmospheric $^{14}\text{CO}_2$, which in 1997 was ~98‰ (Burcholadze *et al.*, 1989; Levin & Kromer, 1997; Levin & Hesshaimer, 2000). If we assume that the isotopic signature of root respiration is the same as that of the atmosphere (Horwath *et al.*, 1994) and that root respiration makes up half of total soil respiration (an approximate average of findings by Raich & Nadelhoffer, 1989), then decomposition and microbial respiration are dominated by material with a $\Delta^{14}\text{C} = 117\%$, or material with a turnover time of about 2 years.

Discussion

Comparing archived soils with modern samples allows an estimation of changes in carbon storage over a

historical period, which cannot be achieved by comparing modern sites alone (Balesdent *et al.*, 1987; Sherbakov & Vaseneva, 1996; Lapenis *et al.*, 2000). Many studies have compared carbon storage under contrasting land uses, such as cultivated vs. uncultivated land, and pasture vs. forest or re-growing forest (e.g., Mikhailova *et al.*, 2000; Veldkamp, 1994; Rodríguez-Murillo, 2001). By assuming that the sites would have the same carbon storage if not for the change in land use, they *can* estimate the impact of conversion on carbon storage. What such studies *cannot* do, however, is quantify change in total soil carbon storage since the land was converted, because both converted and unconverted sites may have been subject to processes that affect carbon storage over the intervening time period. For example, although cultivated soils may have less carbon than nearby uncultivated soils, they may have sequestered C relative to their historic, uncultivated condition due to climatic trends or the planting of hedgerows.

Our results show that there was no detectable difference in carbon storage between 1900 and 1997 soil samples. In the Kamennaya steppe region mean annual precipitation increased during the 20th century. In addition, hedgerow forests planted to prevent wind erosion are likely to have altered evapotranspiration and soil moisture. These climate and management factors may have influenced net ecosystem production or soil carbon cycling, but there was no net influence on soil C storage. Although our analysis is limited to only two points in time and may subsume various source–sink fluctuations during the period (see for example erosion, Harden *et al.*, 1999), these results suggest that comparisons of different land uses in this locale may be used to construct a land use carbon budget over the past century.

Land use impacts on carbon cycling are particularly important in the Russian steppe because, like most of the world's grasslands, this area has undergone almost complete conversion to cultivated land. Within the steppe zone shown in Fig. 1, 65% of the land area was intact, uncultivated grassland in 1863 (Cvetkov, 1957). By the 1990s, about 90% of the historical steppe area was cultivated, and less than 2% remained as steppe or untilld pasture (Milanova *et al.*, 1998).

The carbon and nitrogen content (Table 3) in the top 20 cm of our sites was similar to that measured in other steppe studies or predicted by the Century model for a steppe site (e.g., Parton *et al.*, 1993; Mikhailova *et al.*, 2000). For the whole soil profile, we found comparable stocks to another study that integrated over a meter depth (38.5 kg C/m², Mikhailova *et al.*, 2000), but we report roughly 50% higher soil stocks than other studies (e.g., 18.3 kg C/m², no sampling depth specified, Kolchugina *et al.*, 1995) or than the global estimate for temperate grassland soil C of 20 kg C/m² (Schlesinger,

1997). The difference may be because many studies consider only the upper 20–30 cm, leading to an underestimate of total soil C storage. Extrapolating our results to the region might slightly overestimate historic soil C storage because we sampled only sites of flat relief, which contain more carbon than areas with steeper slopes (Schimel *et al.*, 1985; Harden *et al.*, 1999). In the flat areas of Kamennaya steppe (70–80% of area has slopes less than 5°) the top 10 cm of soil averages 12% C. The slopes of ravines and riverbanks (more than 10°; about 20–30% of the area) contain less than 6–7% C (Ivanov 1991).

The increase in ^{13}C with depth in the 100-year-old soil (i.e., soil collected before extensive fossil fuel emissions) indicates that this pattern with depth is caused by processes other than fossil fuel dilution. In fact, the 2‰ shift in $\delta^{13}\text{C}$ with depth in the 100-year-old archive soil indicates that little of the currently observed ^{13}C pattern is due to the effect of fossil fuel emissions. This suggests that local processes are controlling the fractionation with depth. Deeper carbon, which is older and more stable than shallow organic C, may be enriched in ^{13}C because of downward movement and preferential stabilization of enriched compounds. Organic matter that is stabilized would have enriched $^{13}\text{C}/^{12}\text{C}$ ratios if microbes favor metabolism of the lighter C isotope. Alternatively, there may be favored stabilization of plant tissues or black carbon (partially combusted organic material such as ash or soot) that originate with heavier isotope ratios, either due to isotopic effects on surface chemistry or microbial utilization and transformation of OM. As a confounding influence, however, the history of organic matter burial in loess deposits may also play an important role in the ^{13}C depth profiles (Harden *et al.*, in press). Additional observations of ^{13}C profiles in soils sampled before fossil fuel inputs should be useful in modeling mechanisms of isotopic fractionation.

At the soil surface, the $\delta^{13}\text{C}$ of litter and SOM is 1–1.5‰ lighter in the modern soil than in the archives, presumably from fossil fuel dilution of recent plant inputs. Below about 10 cm, the ^{13}C profiles of the modern and archived soils are similar, indicating that there was little new plant material in the organic matter below that depth. The same picture emerges from the ^{14}C data, in which only the upper layer of the soil shows organic matter from photosynthesis during the past 40 years (i.e., bomb C). Below the surface horizons, the organic matter has the depleted radiocarbon content of older, more recalcitrant material. The steppe soils have extensive bioturbation by mammals (krotovina) that could act to mix surface and deeper soil together, obscuring the signal of recent plant inputs. Nevertheless, the isotope data indicate that a large fraction of SOM in all horizons is highly passive. Similar dominance of recalcitrant C has also been found

from archives of a temperate forest soil (Richter *et al.*, 1999). The origin of the abundant passive (or recalcitrant) C in these soils is not known but is consistent with a recent survey showing large amounts of black C in Chernozems or Mollisols (Schmidt & Noack, 2000). The biogeochemistry of black carbon, its storage, transport, and effects on SOM isotopic signatures, is poorly understood. Harden *et al.* (in press) used ^{10}Be and ^{14}C isotopes to conclude that in similar loessial soils of Iowa, organic carbon was likely incorporated into soil and subsequently buried by accumulating loess. Although these Russian soils have far greater C storage than the Iowa soils, the mechanisms of burial could be similar. Given the ubiquity of loess-derived soils and burning in grasslands, grassland soils may contain more organic carbon than previously estimated, with much of it being recalcitrant and representing long-term storage. Most of the original steppe in Eurasia and North America has been converted to cultivated cropland, and we do not know the fate of the original deep-carbon stocks (Mikhailova *et al.*, 2000). Steppe soils, which have sequestered atmospheric C since the past ice age, may now be a source of C to the atmosphere during the past several hundred years of agricultural expansion (Kolchugina *et al.*, 1995; Sherbakov & Vaseneva, 1996).

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Corrigendum

In the paper by Torn *et al.* Organic carbon and carbon isotopes in modern and 100-year-old-soil archives of the Russian Steppe, 10, 941–953, some data points in Fig. 5(a) were printed incorrectly. The corrected figure is reproduced here.

